# ESTIMATING THE AIR EMISSIONS OF CHEMICALS FROM HAZARDOUS WASTE LANDFILLS*

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## Summary

This paper sets out to develop a comprehensive landfill cover vapour transport model capable of assessing the diffusive and convective transport mechanisms for toxic chemical air emission calculations. Sample calculations of rates for worst-case scenarios involving 4 selected compounds provide some insight into the magnitude of the environment impact of an insecure chemical waste landfill on the surrounding air quality. An algorithm is presented for obtaining crude exposure levels.

## Introduction

In the interest of assessing the environmental impact of an existing or a proposed hazardous waste landfill or similar chemical disposal site, chemodynamic calculations need be made to estimate the emission of volatile chemicals from the surface into the overlying air. A secure landfill is claimed to be the cheapest environmentally sound disposal method available for most hazardous wastes, but of the 100 or so commercial sites in the United States that dispose of, or treat, hazardous waste, the Environmental Protection Agency rates only 20 or so as "secure" landfills that prevent environmental contamination. When contamination questions are confronted rarely are the emission of volatiles, other than methane, considered. Cheremisinoff et al. in 1979 [1] report, in a brief summary of the Love Canal incident, that airborne contaminants were present in concentrations 250 to 5,000 times higher than normal background levels. Air monitoring stations revealed such compounds as chloroform, benzene, trichloroethane, toluene, pentachloroethene, 1,3,5-trichlorobenzene and others.

Volatile chemicals have been stored in landfills. It has been reported [2] that an operator was convicted of saturating dry garbage with toxic chemical wastes and hauling the contaminated garbage to landfills intended only for municipal garbage.

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The design of most of the landfills now in use is not inherently bad. In essence, the approach is to construct an impoundment such that any liquids contained within cannot get out and external waters such as rain and groundwater cannot get in. In practice, this is achieved by enclosing the wastes in a basin with walls, bottom and cap constructed of three meters or more of very dense clay. Such a vault should be very secure if it is not breached. Unfortunately, breaches seem not to be rare. An undiscerned crack in the clay cap, for example, can provide a much less resistant pathway for the migration of chemicals.

A particular site in Hempstead County, Arkansas, was claimed to be well suited for a landfill because of the dense clay soil. Further, it has been maintained that the clay is so impermeable that water can move through the clay at a rate of about 1.2 inches every 1000 years. On the other hand, it was observed that: "water does not stand on the proposed site after a rain and when the clay dries the cracks may go all the way down to the waterline". Although clay is a very good water barrier, it frequently cracks when dry and then becomes a very poor vapor barrier. Earthquakes and other natural phenomena can produce cracks in the vault after it is sealed. Man's activities can also destroy the vault's integrity, as apparently was the case at Love Canal.

The potential air pollution aspects of land disposal of toxic waste have been reviewed recently by Shen and Toffelmire [3]. This paper reviews the subject in general, presents existing models and methods for chemical volatization and landfill gas production. The authors also consider the effect of landfill gas production by microbial fermentation as a mechanism of toxic vapor release and state that without adequate field data on gas production, air pollution problems cannot be fully assessed. In order to determine if under various conditions the levels of toxic vapor released from the landfill are truly significant, this mechanism should be considered.

Farmer et al. [4] have developed a model and predictive equations for use in designing landfill covers based on the vapor phase transport of chemical species through a soil cover to the surrounding atmosphere. The model is based upon experimental results obtained on hexachlorobenzene containing industrial waste (Farmer et al. [5]). The laboratory study of the volatilization flux through a soil cover revealed that soil air-filled porosity was effected by soil compaction and water content and these parameters were important in controlling vapor movement. The model developed by Farmer and co-workers did not account for the effect of landfill gas production.

The goal of this paper is to develop a comprehensive landfill cover vapor transport model capable of assessing the diffusive and convective transport mechanisms for toxic chemical air emission calculations. Sample calculation results of rates for worst-case scenarios involving four selected compounds provide some insight into the magnitude of the environmental impact of an insecure chemical waste landfill on the surrounding air quality. An algorithm is also presented for obtaining crude exposure levels.

## Transport model development

### (a) Landfill without internal gas generation

For purposes of model development, a reservoir of volatile chemical A will be assumed to be present in a subterranean chamber at its pure component vapor pressure or at one atmosphere of pressure. Figure 1 is a cross-sectional view of the fill cell containing drums of the material. This particular illustration depicts the volatile chemical in fifty-five gallon drum containers which are not expected to last three years in the soil. Upon failure of the primary container (55 gal. drums) the pore spaces within the sand-filled chamber will become filled with chemical vapors.
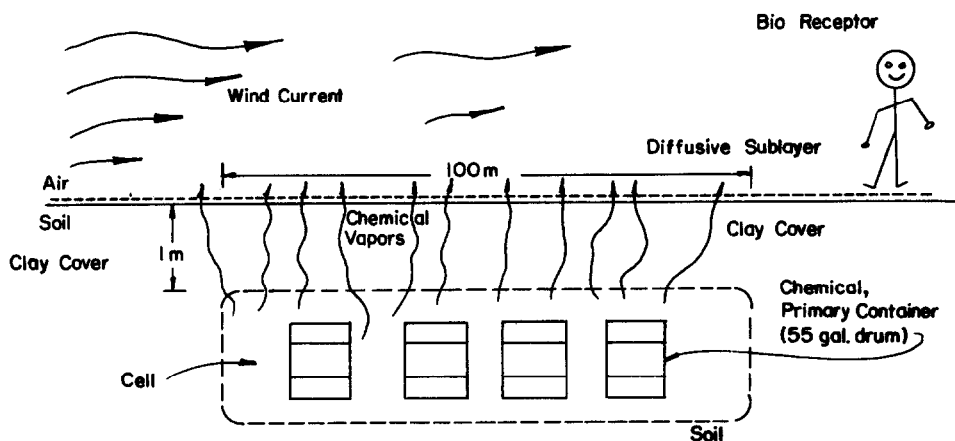


Fig. 1. Chemical vapor movement in hazardous wast landfill.

Chemical vapors originating in the sand-filled chamber move upward through the clay cover and toward the air—soil interface by molecular diffusion through the interconnected cracks and/or pore spaces (see Thibodeaux [6]). The rate of movement within the soil phase is

$$n_A = \frac{D_{A3}}{h} (\rho^*_{A1} - \rho_{A1i}) \tag{1}$$

where $n_A$ is the mass flux rate [$M/L^2t$], $h$ is the depth of the fill cover [L], $\rho^*_{A1}$ is the concentration of A in the sand-filled chamber pore spaces [$M/L^3$], $\rho_{A1i}$ is the concentration of A at the air—soil interface [$M/L^3$] and $D_{A3}$ is the effective diffusivity of chemical A within the pore spaces [$L^2/t$]. The effective diffusivity is known to be a complex function of soil type, soil condition, water content and direction of movement, temperature, porosity, chemical type, etc., however the following simple expression will be used to characterize the long-term value:

$$D_{A3} = \mathcal{D}_{A1} \epsilon / \tau_h \tag{2}$$

where $\mathcal{D}_{A1}$ is the molecular diffusivity of chemical A in air $[L^2/t]$, $\epsilon$ is the porosity (connected) of the cover material, and $\tau_h$ is the tortousity. A value of $\sqrt{3}$ will be used for $\tau_h$.

Vapors moving from the air—soil interface to the overlying air may be described by a rate equation of the form:

$$n_A = {}^3k_{A1}(\rho_{A1i} - \rho_{A1}) \tag{3}$$

where $\rho_{A1}$ is the concentration of A in the air well away from the interface $[M/L^3]$ and ${}^3k_{A1}$ is the gas phase mass-transfer coefficient $[L/t]$. The mass-transfer coefficient may be estimated from a correlation developed by Mackay and Matsugu [7]:

$$^3k_{A1} = 0.0292 V_x^{0.78} L^{-0.11} Sc^{-0.67} \tag{4}$$

where ${}^3k_{A1}$ is the coefficient in m/h, $V_x$ is the wind speed measured at 10 m in m/h, $L$ is the length of the ground emission source in m, and $Sc$ is the Schmidt number for the gas.

By defining an overall soil phase mass-transfer coefficient, ${}^1K_{A3}$,

$$n_A = {}^1K_{A3}(\rho_{A1}^* - \rho_{A1}) \tag{5}$$

it is possible to relate the three coefficients by

$$1/{}^1K_{A3} = 1/{}^1k_{A3} + 1/{}^3k_{A1} \tag{6}$$

where ${}^1k_{A3} \equiv \mathcal{D}_{A1}\epsilon/h\tau_h$. Equations (4)—(6) now provide a means of calculating the flux rate from the fill area.

Chemical concentration at the air—soil interface, $\rho_{A1i}$, may be estimated by using eqn. (1) once $n_A$ is obtained. For the purposes of estimating chemical concentrations in the air above the soil surface, a crude model, consisting of a laminar sublayer and a turbulent zone above, will be used. More realistic (and complex) models may be developed by employing recent deposition velocity correlations used for sulfur dioxide [8].

The concentration across the diffusive sublayer may be estimated by:

$$n_A = \frac{\mathcal{D}_{A1}}{\delta_{A1}} (\rho_{A1i} - \rho_{A1}|_{\delta_{A1}}) \tag{7}$$

where $\rho_{A1}|_{\delta_{A1}}$ is the concentration at the upper edge of the diffusive sublayer $[M/L^3]$ and $\delta_{A1}$ is the sublayer thickness $[L]$ obtained from:

$$\delta_{A1} = 26\nu_1/V_* Sc^{1/3} \tag{8}$$

where $\nu_1$ is the kinematic viscosity of air $[L^2/t]$ and $V_*$ is the friction velocity $[L/t]$.

The Prandtl mixing length model analogy for turbulent diffusion may be

used for estimating concentrations in the region above the sublayer:

$$\rho_{A1} = \rho_{A1}|_{\delta_{A1}} - \frac{n_A}{K_1 V_*} \ln (y/\delta_{A1}) \tag{9}$$

where $K_1$ is Prandtl's constant (0.4) and $y$ is the distance above the air—soil interface [L].

Equations (7)—(9) can be used to obtain crude estimates of chemical concentrations in the air space above the landfill area.

### (b) Landfills with internal gas generation

Due to biogenic processes (anaerobic degradation) within the cells of solid waste, landfill gas (mostly $CO_2$, $H_2$ and $CH_4$) is produced and moves upward toward the surface [9]. In addition to molecular diffusion there is a convective "sweep" of the chemical toward the surface by this moving gas. Chemical movement within the cover material is now described by the equation

$$D_{A3} \frac{d^2\rho_{A1}}{dy^2} - V_y \frac{d\rho_{A1}}{dy} = 0 \tag{10}$$

with boundary conditions, $\rho_{A1}^*$ at $y = 0$ and $\rho_{A1i}$ at $y = h$, where $V_y$ is the mean gas velocity in the pore spaces [L/t]. The solution of eqn. (10) is:

$$\rho_{A1} = \rho_{A1}^* - (\rho_{A1}^* - \rho_{A1i}) \left\{ \frac{1 - \exp (yV_y/D_{A3})}{1 - \exp (hV_y/D_{A3})} \right\} \tag{11}$$

The flux expression, which contains a diffusive and a convective term and is:

$$n_A = V_y \frac{(\rho_{A1}^* - \rho_{A1i})}{\exp (hV_y/D_{A3}) - 1} + V_y \rho_{A1}^* \tag{12}$$

Equation (12) reduces to eqn. (1) when $V_y$ is zero since

$$\lim_{V_y \to 0} \{\exp (hV_y/D_{A3}) - 1\} = hV_y/D_{A3} \tag{13}$$

The interface concentration for case (b) may be obtained by solving eqns. (11) and (12) simultaneously. Chemical concentrations above the air—soil interface for this case are estimated as in case (a).

### Integrated exposure

Workers, nearby residents and others are exposed to the vapors escaping from the landfill or disposal area. Behar et al. [10] have defined an

integrated exposure measure to assess the impact of a pollutant upon a biota via a variety of pathways:

$$E_{ijk} = \int_{t_1}^{t_2} S_{ik}(t)P_{jk}(t)D_i(t)\,\mathrm{d}t \tag{14}$$

where $E_{ijk}$ = the exposure from the $i$th pollutant from $t_1$ to $t_2$ via pathway $j$ to receptor at location $k$, $S_{ik}$ = the time-dependent source strength of $i$ at $k$, $P_{jk}$ = the pathway transfer function for pathway $j$ and location $k$, $D_i$ = the exposure rate for pollutant $i$.

$$R_{ijk} = (E_{ijk})f(T_i) \tag{15}$$

where $R_{ijk}$ = the relative risk assessment and $f(T_i)$ = toxicity of the $i$th pollutant.

For the case of volatile chemical emissions from landfills nearby residents are continually exposed to the pollutant vapors which may be for the lifetime of the landfill so $t_2 - t_1$ is the order of ten years. The time dependent source strength in this case is taken to be the air concentration at the 1.5 m level above the air—soil interface as determined by eqn. (9). The pathway transfer function is the fraction of the time the wind direction is from the landfill toward the receptor. The exposure rate in this case is the rate of inhalation of air by the receptor ($Q$ = 4 l/min). The relative risk involved by the receptor can now be established by eqns. (14) and (15) once the toxicity function is known. Evaluation of $f(T_i)$ is beyond the scope of this paper; however, the yearly exposure can be obtained from:

$$E_{A,air} = \rho_{A1}(y = 1.5\text{ m}) \times 1 \times Q \tag{16}$$

where the maximum pathway transfer function of unity is used.

**Calculated emission and exposure rates for selected chemicals**

For the purpose of demonstrating the calculation technique and establishing order of magnitude estimates, the emission and exposure rates of four common industrial chemicals are computed. The chemicals are benzene, chloroform, vinyl chloride and a polychlorinated biphenyl (Aroclor 1248). Chemical properties at 25°C are given in Table 1. The following environmental parameters were chosen and remained constant for each chemical calculation: temperature $T$ = 25°C, wind speed $V_x$ = 8.2 mi/h, friction velocity $V_*$ = 0.5 m/s, porosity of cover $\epsilon$ = 0.51 and tortousity $\tau_h$ = 1.73.

Internal gas "sweep" velocities were estimated from data reported by DeWalle and Chian [9] for pumped extraction wells. For the Palos Verdes landfill a maximum test flow of 56 ml/kg·d from a fill of dry density 714 kg/m$^3$ of 33.5 m depth with assumed cover porosity of 0.51 yielded a 3.04E − 3 cm/s velocity. For the Sheldon Arleta landfill a gas production

TABLE 1

Chemical properties at 25°C

| Chemicals | Formula | Molecular weight | Vapor pressure (atm) | Diffusivity in air, $\mathcal{D}_{A_1}$ (cm$^2$/s) |
|---|---|---|---|---|
| Benzene | C$_6$H$_6$ | 78.1 | 0.125 | 0.088 |
| Chloroform | CHCl$_3$ | 119.4 | 0.263 | 0.104 |
| Vinyl chloride | CH$_2$CHCl | 62.5 | 1.0$^\dagger$ | 0.127 |
| Aroclor 1248* | C$_{12}$H$_6$Cl$_4$ | 292.0 | 4.94E − 4 | 0.048 |

$^\dagger$Vinyl chloride is a gas at 25°C.
*a PCB

rate of 22 ml/kg·d from a fill of dry density 595 kg/m$^3$ of 38 m depth with assumed cover porosity of 0.51 yielded a 1.13E − 3 cm/s velocity. For the Mountain View landfill a gas production rate of 45 ml/kg·d from a fill of dry density 595 kg/m$^3$ of 12 m depth with assumed cover porosity of 0.51 yielded a 7.29E − 4 cm/s velocity. The average velocity for the three landfills but vary considerably with time, with location within the landfill, internal gas generation, this average velocity will give a representative upper bound for the un-pumped case. In reality, flow rates are not constant in landfills but vary considerably with time, with location within the landfill, and with temperature, moisture content, type and age of the refuse.

Results of the calculation appear in Table 2. These emission rates and parameters represent a landfill area of 100 m × 100 m surface area with a cover depth of 1 m. Data are presented for each chemical both with and without gas generation in the fill. Selected transport parameters, concentrations and emission rates are presented in order to understand the chemical movement mechanism.

The first row of data contains the effective diffusivity values for diffusion through the fill cover pore spaces. The calculated values range from approximately 0.01 to 0.04 cm$^2$/s. Silker et al. [11] calculated effective diffusivities for radon ($^{222}$Rn) from concentration profiles in uranium mill tailings piles and report values of 0.0017 cm$^2$/s for 5% H$_2$O moisture content and 0.0002 for 15% H$_2$O moisture content. A review of published literature by Silker et al. yielded reported effective diffusivities of 0.05 and 0.004 cm$^2$/s for uranium tailings, 0.07 for sand and 0.005 to 0.068 cm$^2$/s for fine quartz. Values used in these landfill calculations fall within the upper range of the reported values.

Rows two through four are calculated mass-transfer coefficients for the fill cover layer (soil), air phase and the overall respectively. In all cases the fill cover layer provides the major resistance to the movement of chemical vapors from the fill cells into the overlying air. The generation of gas within the cells with escape through the cover to the surface has a major influence

TABLE 2

Emission Rates from Hazardous Waste Landfills

| | Benzene | | Chloroform | | Vinyl chloride | | Aroclor 1248 | |
|---|---|---|---|---|---|---|---|---|
| $V_y =$ | 0.0 | 1.63E − 3 | 0.0 | 1.63E − 3 | 0.0 | 1.63E − 3 | 0.0 | 1.63E − 3 |
| 1. $D_{A_3}$ (cm²/s) | 0.0259 | 0.0259 | 0.0307 | 0.0307 | 0.0374 | 0.0374 | 0.0142 | 0.0142 |
| 2. $^1k_{A_3}$ (m/h) | 9.34E − 3 | 59.0E − 3 | 11.0E − 3 | 59.1E − 3 | 13.5E − 3 | 59.6E − 3 | 5.09E − 3 | 58.9E − 3 |
| 3. $^3k_{A_1}$ (m/h) | 20.14 | 20.14 | 22.53 | 22.53 | 25.80 | 25.80 | 13.40 | 13.40 |
| 4. $^1K_{A_3}$ (m/h) | 9.33E − 3 | 58.8E − 3 | 11.0E − 3 | 58.9E − 3 | 13.5E − 3 | 59.5E − 3 | 5.09E − 3 | 58.6E − 3 |
| 5. $\delta_{A_1}$* (cm) | 0.0653 | 0.0653 | 0.0690 | 0.0690 | 0.0738 | 0.0738 | 0.0534 | 0.0534 |
| 6. $\rho_{A_1}$* (g/m³) | 399.3 | 399.3 | 1284. | 1284. | 2556. | 2556. | 7.76E − 3 | 7.76E − 3 |
| 7. $\rho_{A_1}$ (g/m³) | 0.185 | 1.165 | 0.629 | 3.360 | 1.340 | 5.900 | 2.95E − 6 | 3.39E − 5 |
| 8. $\rho_{A_1}$ @ $\delta_{A_1}$ (g/m³) | 0.108 | 0.682 | 0.368 | 1.970 | 0.781 | 3.450 | 1.72E − 6 | 1.99E − 5 |
| 9. $\rho_{A_1}$ @ 150 cm (g/m³)† | .0681 | 0.429 | 0.216 | 1.160 | 0.417 | 1.840 | 1.29E − 6 | 1.49E − 6 |
| 10. $n_A$ (g/m²·d) | 89.4 | 563. | 340. | 1820. | 826. | 3650. | 9.49E − 4 | 109E − 4 |
| 11. $E_{A,air}$ (g/y) | 1430. | 9023. | 4550. | 24300. | 8770. | 38700. | 0.0271 | 0.312 |

†$\rho_{A_1}$, background of 0.0 g/m³ used in calculations.

upon the effective soil-phase mass-transfer coefficient. The coefficient increases approximately seven times as the gas velocity changes from zero to 1.63E − 3 cm/s. Rows six through nine map the decrease in the chemical concentration in air from the cell pore spaces, through the fill cover layer across the laminar boundary layer (thickness given in row 5) and into the turbulent zone to the 1.5 meter position. The most significant decrease occurs across the 1 meter of fill cover material where the concentration is reduced by a factor of 350 to 2200 for the cases with and without internal gas generation. The concentrations at 1.5 meters above the air-soil interface (row 9) represent the likely maximum exposure level encountered by workers, residents and others in the near area of the hazardous waste landfill. Row 9 is the calculated emission flux rates for each chemical in $g/m^2 \cdot d$ and row 10 is the integrated yearly exposure in grams. By way of comparison Silker et al. [11] report radon exhalation rates of 60 to 275 atoms/ $cm^2 \cdot s$ which correspond to a emission flux rates of 1.9E − 11 to 8.8E − 11 $g/m^2 \cdot d$. The chemical flux rate increases by a factor of seven for a gas generated velocity of 1.63E − 3 cm/s.

There is a very limited amount of data available to verify this model. Table 3 presents some model verification results based on the hexachlorobenzene data obtained by Farmer et al. [5]. This verification is for the vapor phase diffusion model (eqn. (1)) only. The general flux model (eqn. (12)), which accounts for convective gas movement, has not been verified.

TABLE 3

Model verification data — hexachlorobenzene (Farmer et al., 1976)

| Topsoil depth (cm) | Measured flux (kg/ha· yr) | Calculated from eqn. (1) flux (kg/ha·yr) |
|---|---|---|
| 1.9 | 4.56 | 17.4[†] to 0.867* |
| 30.5 | <0.1 | 1.08[†] to 0.0538* |
| 120.0 | 0.066 | 0.275[†] to 0.0137* |

[†]$\epsilon = 0.51$, $\tau_h = 1.73$
*$D_{A_3} = 0.0017$ cm²/s for $^{222}$Rn in tailings.

## Conclusions

A simple model for the movement of chemical vapors and gases from the cells of a hazardous waste landfill or similar subterranean disposal site into the overlying air-space has been developed. Based upon calculations with four representative chemicals the following can be concluded:

1. Vapors and gases can escape from the cells and contaminate the air space near the landfill. The rate of escape and the degree of air contamina-

tion increases as the chemical vapor pressure increases and as gas is produced by biogenic processes within the cells.

2. The fill cover layer provides an effective vapor barrier reducing the air concentration by a factor 350 to 2200. Chemical movement from the cells is retarded primarily by transport through the fill cover layer.

3. Calculated concentration levels, flux rates and integrated yearly exposure levels likely represent maximum values for these chemicals. Variable wind directions, receptor movements, deeper fill cover layers, water saturation of pore spaces, soil compaction, air turbulence, and personnel safety factors will likely operate to lower the actual exposure to individuals significantly.

A secure primary container (steel drum, solidification, encapsulation, etc.) for volatile chemicals will stop any movement of vapors or gases to the air-soil interface and eliminate the exposure hazard. An insecure primary container will release the chemical to the cells and diffusion/convective transport processes will move the chemical to the air—water interface where exposure to receptors can be significant.

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